

APPLICATION OF SCANNING ELECTRON MICROSCOPY AND AUTOMATED IMAGE ANALYSIS FOR CHARACTERIZATION OF MINERAL MATTER IN COAL

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INTRODUCTION

The value of the scanning electron microscopy in providing in-situ information on the microstructure of materials such as coal is well known. It is particularly suited for examining the finely distributed mineral particles found in finely-ground coal. In polished cross section, a wealth of size, shape, roughness, and association data can be provided. Addition of an energy-dispersive x-ray analyzer permits chemical analysis to be performed on these minute features, thus allowing a tentative identification of the mineral phase.

The use of automated image analysis (AIA) in conjunction with scanning electron microscopy (SEM) and energy-dispersive x-ray analysis (EDX) is gaining ever wider acceptance as a powerful tool for the in-situ characterization of mineral matter in coal (1). The SEM-AIA technique is able to combine data from SEM and EDX measurements to provide detailed information on sample character that is not available from other analytical methods. The unique features of AIA include information generated for size, shape, composition, and association of mineral phases with the coal matrix.

The SEM-AIA technique is applicable to a wide variety of characterization problems. Because the in-situ nature of this capability can provide quantitative information on the distribution of the mineral species present in coal, it lends itself particularly well to the characterization of minerals in raw and processed coals. Distribution of minerals by both phase and particle size is of great importance to almost any work on coal, but it is especially useful to coal plant operators in determining the steps necessary for effective and efficient removal of undesirable mineral phases during cleaning (2). It is not adequate to know only the relative amounts of the mineral phases present; such information is available from x-ray diffraction or infra-red spectroscopy. But the size of the minerals and their relation to the coal matrix is just as important. Such information was provided in a recent publication of our studies (3). In that work, the mineral matter distribution in raw coals and coals supercleaned by float-sink techniques was described.

In this work, the SEM-AIA technique as an analytical method for coal will be described. The discussion will include particle detection and measurement, mineral phase identification by x-ray analysis using a file of chemical definitions, and the number of particles needed to develop reliable results and adequate reproducibility between samples. In addition, attention will be given to problems in the application of AIA techniques to coal, including difficulties arising from a wide spread in the minimum and maximum particle sizes, problems in the apparent enrichment of pyrite content due to instrumental factors, and the special case of characterizing chemically treated coals.

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The SEM-AIA techniques have been applied at the Ames Laboratory to many samples of bituminous and sub-bituminous coals to characterize their mineral content for studies of cleanability. Results from some of those studies will be used to illustrate the application and limitations of this technique.

BACKGROUND

Combined SEM-EDX techniques have been able to provide much information with manual operation, but results were qualitative and subject to operator judgment. The development of automated control for the SEM has permitted the same information to be extracted objectively, quantitatively and less tediously. The main limitation of the manual techniques is the human factor, since the analysis of particles for size and elemental composition is tedious. Human operators are severely limited in the rate and amount of data that they can reasonably produce. There is also a possibility of operator bias in not treating all particles alike. The intelligence of a human operator is a fantastic advantage, but the limitations on the operator are also significant.

The task of the automated image analyzer is to assume the repetitive duties of the SEM operator in such a way that statistically significant number of particles can be analyzed in a reasonable amount of time and to tabulate the data in a meaningful format. The following paragraphs describe the operations involved.

The first requirement of particle characterization is feature identification and sizing. A human operator is able to work with gross signal contrast and rather subtle edge effects to determine feature outline. As a rule, the microcomputers and electronics used in image analysis in the lab are presently restricted to determining particle boundaries, or extents, from the rather gross measure of contrast in the signal level. Therefore, sufficient contrast is required in the video signal between two phases of interest to permit differentiation of the phases. Backscattered electron imaging is very sensitive to the average atomic number of a phase and, therefore, provides high contrast between minerals of relatively high atomic number and lower atomic number coal and mounting material. A specialized analog-to-digital converter, called a "threshold selector," is used to inform the computer which pixels are above threshold and belong to a phase of interest, and which pixels are below threshold and therefore indicate background phase. The computer is thus able to discern which picture elements belong to coal, mineral, or background.

The mode of extracting information on the particle extents is complicated. In many image analysis systems built around optical microscopes and TV cameras, the whole image is digitized for processing. For SEM operations this is often not practical. Often the signal from an SEM exhibits a relatively low signal-to-noise ratio requiring that several frames be averaged to provide an adequate signal. Also, some older SEM instruments do not respond well to the scanning speed demands of TV imaging rates. In addition, it is only recently that backscattered electron detectors have become available that can operate at TV-rates. Therefore, it has been common for SEM-based image analyzers to employ some form of digital beam control to direct the beam on the sample in such a fashion as to extract the most information in the least time. A number of software algorithms are available with our AIA system to discern particle extents.

Once the particle extents have been determined, the chemical identity of a particle is determined. The image analyzer directs the SEM beam to the center

of the particle of interest and directs the EDX analyzer to collect an x-ray spectrum. Whereas a human operator can quickly scan the entire x-ray spectrum to locate and identify the significant x-ray peaks, the image analyzer must monitor regions of interest defined about x-ray lines of interest. For many mineral analyses, only 11 common elements are necessary. They are, in increasing atomic number: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, and Fe. Additional elements can be also monitored if they are suspected to occur in trace quantities. Based on the relative intensities of the x-ray signals, particles are classified into one of several mineral categories according to definitions such as those given in Table 1. For many AIA applications, including coal mineral analyses, it is reasonable to define the chemical categories rather loosely and still to discern the various mineral components. In fact, for many minerals, it is necessary only to define the elements that must be present to define a mineral. Quartz and calcite are examples for which only a single element is needed (Si and Ca, respectively). However, for the clay minerals, more sophisticated definitions are necessary to differentiate the phases.

Table 1. Ranges of Elemental Compositions, Ratios, and Other Features for mineral phase definitions.^a

Mineral Phase	Chemical Definition in % Range ^b	Density
Pyrite	S 10-80, Fe 10-70	5.00
Kaolinite	Al 15-80, Si 15-85 Al/Si ratio 0.4-2.5	2.65
Illite	Al 15-80, Si 20-85, Fe 0-40, K 2.5-35, Na 0-20	2.75
Montmorillonite	Al 10-75, Si 19-80, Na 0-30, Ca 0-30	2.30
Quartz	Si 60-100	2.65
Calcite	Ca 70-100	2.80
Minors (included are the following categories)		
Gypsum	S 10-80, Ca 10-70	2.30
Dolomite	Mg 5-60, Ca 60-100	2.90
Iron-rich (e.g. siderite)	Fe 90-100	3.90
Chlorite	Al 10-75, Si 10-80, Mg 0-30, Fe 0-30 (Mg or Fe required)	3.00
Rutile	Ti 70-100	4.50
Al-Rich	Al 75-100	4.00
Apatite	P 10-40, Ca 30-100	3.20
Silicates	Si 40-100	2.70
Miscellaneous	All other elemental compositions not specifically defined	2.00
Not included	Signals with <1000 total x-ray count	

^a Modified after Reference 3.

^b Additional specifications are often given for other elements that are allowed to be present. Although such specifications allow the presence of minor elements not specifically listed in the chemical definition, they place an upper limit on the allowable amount.

EXPERIMENTAL

The AIA-SEM system at Iowa State University consists of a JEOL (Japan Electron Optics Laboratory) model JSM-U3 scanning electron microscope, a LeMont Scientific B-10 image analyzer, and a Tracor Northern TN-2000 energy-dispersive x-ray spectrometer. The software-based AIA system contains associated electronics for SEM beam

control, image amplification, and thresholding. For AIA, the software base allows selection of the appropriate analysis algorithm for the particular sample and image conditions encountered.

Actual analyses were performed on pellets of coal mounted in an epoxy or polyethylene matrix according to standard petrographic procedures. The pellets were polished to a cross section and coated with carbon to render the surface electrically conductive for SEM examination. Samples were analyzed in the SEM under 50-500x magnification, using 25 kV beam voltage, 1-2 nA sample currents, and backscattered electron imaging. A point density of 1024 pixels across the screen was used to provide $\pm 10\%$ accuracy on measurements as small as 1% of the field of view. X-ray data were collected for four seconds per particle at a typical rate of 1000 counts per second. The intensities of 30 elements were set to be monitored in regions of interest. Approximately 4000 particles were analyzed per sample, at a rate of 200 particles per hour.

The AIA procedures classify mineral particles into both size and chemical classes. Area-equivalent diameter was used as the size parameter for data presentation. This measurement is the diameter of a circle with the same area as that measured for the mineral particle. Area-equivalent diameter was used instead of a simple length or width measurement because the outline of mineral particles in coal is often complex enough to render such measurements meaningless. The equivalent diameter measurement allows particles to be classified by the area of the particle and yet reported in terms of a linear dimension. Using available literature values for the specific gravity of the individual minerals, the data were then expressed as the weight fraction of the mineral matter within a given mineral/size category. The weight fraction data could then be normalized according to the mineral matter content calculated from ash values by using a modified Parr formula (4) to present mineralogical estimates on a dry coal basis. Such a presentation provides a common base for comparing the coals before and after processing.

DISCUSSION OF RESULTS AND PROBLEMS

A major problem encountered in the analysis of coal samples arose from the wide size range of particles present. The weight distribution is heavily influenced by the particles in the largest size categories. However, most of the particles are found in the smallest categories. This problem is especially troublesome for relatively coarse samples of where the particle diameter can range from 1 to 1000 μm . As an example, Table 2 presents actual data for such a case, using an Illinois No. 6 coal characterized more fully elsewhere (3).

Since analysis time per particle is dominated by the time of x-ray acquisition which is independent of particle size, it becomes necessary to allocate analysis time among the size categories in order to include a significant number of particles of all sizes. Therefore, analyses were conducted at several magnifications for restricted ranges of particle sizes. A relatively small area was analyzed at high magnification to collect data on small particles, and a much larger area was then analyzed at lower magnification to collect data on large particles. Data were then combined by correcting the weight of particles analyzed in each size range for the area of sample analyzed for that size range. The table of weight fractions was then normalized to 100%. For samples with particularly wide size ranges, three or more size partitions were required to obtain a representative size distribution. As can be seen from Table 2, the actual number of particles counted parallels the weight distribution much closer than does the unadjusted count fraction.

Table 2. Weight and Count Distribution for an Illinois No. 6 Coal
(Nominally 70-80% less than 200 mesh or 75 μm)

	Area Equivalent Diameter (in μm)					
	0-4	4-7	7-12	12-20	20-36	>36
Count fraction	16.3	51.1	23.3	7.1	1.7	0.6
Weight fraction	2.5	15.3	20.4	21.0	14.4	26.3
% of particles counted	13.6	42.6	25.3	7.8	7.9	2.8
Number of particles counted	654	2055	1221	374	382	136

The statistical distribution involved in AIA analysis is a multinomial distribution, for which the standard deviation of the counts measured for a category is equal to the square root of the count. Thus a count of 100 particles would yield to a relative standard deviation of 10%. Relative error in the weight distribution results can be calculated from the number of particles collected in each category. For a system of four predominant minerals with approximately equal particle abundances, and six size categories, approximately $4 \times 6 \times 100 = 2400$ particles would be needed for a relative standard deviation of 10% in the data.

This assumption has been borne out in analyses of multiple pellets of the same coal. Five pellets each of three coals were analyzed by AIA. A total of 1500 particles was characterized for each pellet. Standard deviations were calculated from the five estimates of weight fraction in each size/chemical category and compared with the relative error expected from the particle count. Agreement was excellent for categories containing more than ~30 particles.

A problem of artificial enrichment of one phase relative to the others arises when one phase appears much brighter in the image being analyzed than do the remaining phases. In our work with coal minerals (3,5) and in the work of others (6) such a problem was experienced with the mineral pyrite. Typically the pyrite content found by SEM-AIA is substantially higher than what is estimated by the ASTM wet chemical technique (see Table 3). The problem arises in our AIA system since it employs what is known as "global thresholding". In it, a threshold level is established against which image signal levels are compared to determine whether a pixel is part of a particle or part of the background. The recommended procedure is that the threshold be set midway between background and full signal brightness to allocate equally any noise on the particle edges between particle and background. For coal minerals this is strictly not possible. The intensity of backscattered electron image used for analysis is highly dependent on the average atomic number of the material in view. Pyrite is so much heavier than the other mineral phases that the threshold, set at a level at which the clays can be consistently detected, crosses pyrite particles at the 20-30% level and increases the possibility that individual pyrite particles will be measured larger than they are. To compensate for this bias, the U.S. Steel workers (6) recommended an empirical factor of 0.75 for scaling down the pyrite values.

Another possible explanation is that the brighter signal for pyrite causes small particles of the mineral to have a better chance of rising above threshold as opposed to the signal being diminished to a level below the threshold by the fact that a large percentage of the electrons pass completely through the particle before backscattering, causing the signal brightness to be lower than the signal from a massive particle. However, this explanation does not account for much of the error

observed since only a relatively small amount of the pyrite is found in the smallest size ranges.

Table 3. Comparisons of ASTM and SEM-AIA Estimates of Pyrite and Pyritic Sulfur Sulfur Content for Raw and Supercleaned Coals (recalculated from data of Reference 3)

	Illinois No. 6		Pittsburgh No. 8	
	Raw	Cleaned	Raw	Cleaned
<u>Pyritic Sulfur</u>				
ASTM	2.37	0.22	1.35	0.03
AIA	4.22	0.63	2.50	0.52
<u>Pyrite/Mineral Matter^a Ratio</u>				
ASTM	22.93	13.48	30.55	1.66
AIA	40.86	38.53	56.54	28.59
Fe by XRF (%)	2.01	0.38	1.64	0.44
Total S (ASTM)	5.10	2.54	3.17	1.82
Organic S (ASTM)	2.36	2.27	1.42	1.67
Mineral Matter ^a	19.32	3.05	8.26	3.37

^a Mineral matter = 1.13 (ash) + 0.47 (pyritic sulfur), as in reference 4.

For chemically processed coals, problems arise with the chemistry definitions. New mineral phases may be formed during processing that bear little resemblance to the original minerals. It may become necessary to analyze the material with alternate techniques, such as x-ray diffraction, in order to determine what phases are present. Then the necessary chemical definition can be built into the file knowing the chemistry of the new phases. Alternatively, an automatic classification option can be employed to sort particles routinely based on the relative amounts of the elements present.

Some of our work with the direct determination of organic sulfur in raw and chemically treated coal by an SEM-EDX technique (7) and additional analysis of mineral matter in those samples by FTIR spectroscopy (8) indicate that the AIA values for pyrite may be correct for at least some samples. The analyses were performed on samples of Illinois No. 6 coal, raw and chemically cleaned by the Gravimelt Process at TRW Inc., in California (8). The samples were analyzed by ASTM techniques for moisture, ash, and sulfur forms; by SEM-AIA for mineral phases; by SEM-EDX for organic sulfur; and by FTIR for mineral phases. The results are presented in Tables 4 and 5.

For the raw coal, the pyritic sulfur values obtained by AIA agreed well with those obtained at TRW. However, they were somewhat higher than the ASTM values obtained at Ames. For the cleaned coal, the pyrite values obtained by AIA and the organic sulfur values obtained by SEM agreed very well with the Ames ASTM results.

The comparison of FTIR data with AIA results in Table 5 shows good agreement for all components except kaolinite. Since the coal had to be low-temperature ashed for the FTIR analyses, and the cleaned coal did not have much ash left, the FTIR results on the cleaned coal are not as informative as the AIA results. The FTIR techniques could not identify much of the mineral matter in the cleaned coal, adding most of it

to the miscellaneous category. Since AIA does not require mineral standards and is not particularly dependent on crystal structure, more particles could be categorized by the chemical definition file.

Table 4. Analysis of Illinois No. 6 Treated by the Gravimelt Process at TRW
(Values reported as wt. % on a dry basis, except for moisture)

	RAW COAL			TREATED COAL		
	TRW Results	ASTM At Ames Lab	SEM/AIA Results	TRW Results	ASTM At Ames Lab	SEM/AIA Results
Moisture	15.81	1.84	----	----	6.33	-----
Ash	9.97	9.23	----	0.51	0.53	-----
Mineral Matter ^a	-----	10.92	----	----	0.61	-----
Total S	4.21	4.03	----	0.57	0.59	-----
Pyritic S	1.36	1.04	1.46	----	0.02	0.026
Sulfate S	0.05	0.09	----	----	0.02	-----
Organic S	2.80	2.90	2.13	----	0.35	0.32

^a Mineral Matter = 1.13 (ash) + 0.47 (pyritic sulfur), as in reference 4.

Table 5. FTIR and AIA Results of Raw and Chemically Treated Illinois No. 6 Coal
(values expressed as wt. % of total mineral matter present)

	RAW		TREATED	
	FTIR	AIA	FTIR	AIA
Kaolinite	12.0	7.4	4.0	8.4
Illite	31.5	29.8	----	10.2
Quartz	19.0	20.0	10.0	13.9
Calcite	1.5	1.3	----	3.7
Pyrite	----	23.3	----	8.4
Miscellaneous	36.0	18.1	86.0	46.0

In addition, the AIA technique provided information on particle size distribution as well as mineral phase identification (see Table 6). Such information, of course, cannot be provided by the FTIR technique.

CONCLUSIONS

The SEM-AIA technique has been shown to be a useful tool in characterizing the mineral matter of coal by chemical composition as well as particle size distribution. The fundamental aspects of this analytical technique have been described, including the method of defining mineral phases by chemical composition, requirements for the number and size of particles to be samples for reliable and reproducible results, comparison of this technique with other methods of characterizing coal mineral matter, and some problems associated with the application of this technique to measurements of pyrite and analysis of chemically treated coals.

TABLE 6. AIA Classification of Mineral Matter in Illinois No. 6 Coal by Chemistry and Area-Equivalent Diameter of Particles (in μm), Expressed as Weight Percent of the Total Mineral Matter Only.

Mineral Phase	<u>Raw Coal</u> Particle size (μm)						Total ^a
	< 6.3	6.3-19	20-62	63-199	200-632	>632	
Pyrite	2.16	7.97	7.02	6.14	0.00	0.00	23.29
Kaolinite	1.34	3.81	1.52	0.70	0.00	0.00	7.37
Illite	4.27	7.29	4.90	5.08	8.28	0.00	29.82
Quartz	4.47	9.15	3.95	1.98	0.51	0.00	20.06
Iron-rich	0.04	0.22	0.49	1.16	0.00	0.00	1.91
Calcite	0.05	0.06	0.08	0.21	0.92	0.00	1.32
Silicates	1.57	2.19	1.38	1.47	0.98	0.00	7.59
Miscellaneous	1.64	4.13	0.70	0.40	1.73	0.00	8.60
Total ^a	15.54	34.83	20.04	17.15	12.42	0.00	100.00

Mineral Phase	<u>Clean Coal</u> Particle size (μm)						Total ^a
	< 6.3	6.3-19	20-62	63-199	200-632	>632	
Pyrite	2.74	4.54	1.09	0.00	0.00	0.00	8.37
Kaolinite	4.20	3.35	0.89	0.00	0.00	0.00	8.43
Illite	5.78	4.41	0.00	0.00	0.00	0.00	10.19
Quartz	6.82	6.42	0.67	0.00	0.00	0.00	13.91
Iron-rich	1.93	2.66	0.00	0.00	0.00	0.00	4.59
Calcite	1.63	2.06	0.00	0.00	0.00	0.00	3.69
Silicates	1.71	2.50	0.64	0.00	0.00	0.00	4.85
Miscellaneous	14.34	21.60	10.03	0.00	0.00	0.00	45.97
Total ^a	39.15	47.53	13.32	0.00	0.00	0.00	100.00

^a Totals may be slightly off due to rounding.

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